

Supporting information for the paper:

**Switchable Aerobic/Anaerobic Multi-Substrate Biofuel Cell Operating
on Anodic and Cathodic Enzymatic Cascade Assemblies**

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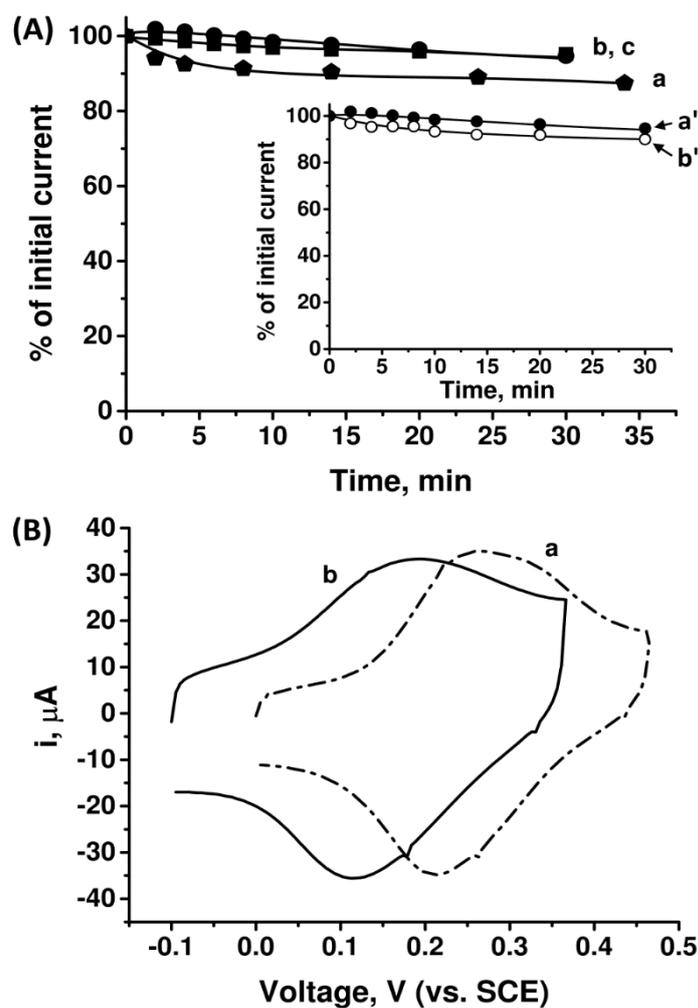


Fig. S1 (A) Time-dependent relative current responses recorded for the mediators: (a) FcM, (b) TTF, and (c) ABST²⁻, loaded in MCP-modified GC electrodes and capped by CAT following the immersion of the electrodes for variable time-intervals in a N₂-purged Mcllvaine buffer solution. The relative values were derived by periodically performing cyclic voltammetry at 100 mV s⁻¹ and indicate the peak currents obtained at E=0.25 V, E=0.20 V, and E=0.50 V vs. SCE for the mediators (a)-(c) respectively, relative to the initial currents obtained before immersion of the electrodes. Inset: comparison between the time-dependant relative current responses of TTF in: (a') N₂-purged, and (b') O₂-purged Mcllvaine buffer solutions. (B) Cyclic voltammograms corresponding MCP-modified GC electrodes which were loaded with: (a) FcM, and (b) TTF, and capped by CAT. Scan rate: 100 mV s⁻¹. Experiments were performed in a N₂-purged Mcllvaine buffer solution.

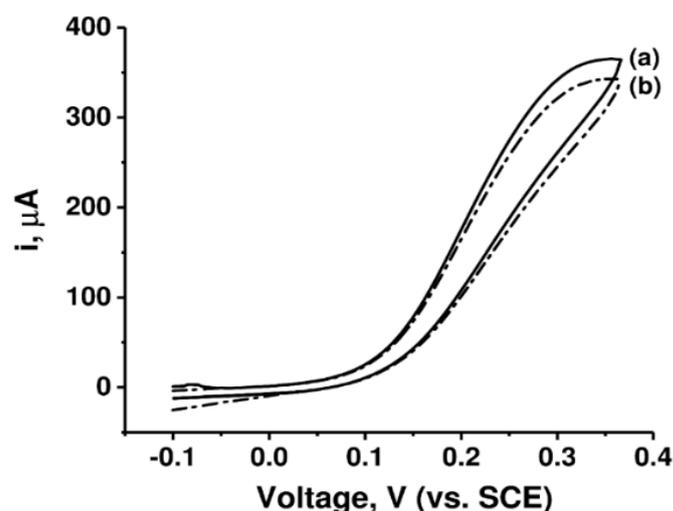


Fig. S2 Cyclic voltammograms demonstrating anodic bioelectrocatalytic currents obtained following the exposure of the INV/MUT/GOX/FDH-cascaded anode for 10 minutes to McIlvaine buffer solutions containing 100 mM of glucose, 100 mM of fructose, and 180 mM of sucrose: (a) in the absence of H_2O_2 , and (b) in the presence of 140 mM H_2O_2 . All measurements were performed at a scan rate of 20 mV s^{-1} . A 60 minutes N_2 purging was applied to the cell.

INV	x	x	x	x		x	x	x				x			
MUT	x	x		x	x	x			x	x			x		
GOX	x	x	x		x		x		x		x			x	
FDH	x		x	x	x			x		x	x				x
I_p, μA	43 ± 4	25 ± 4	26 ± 2	18 ± 3	9 ± 2	0 ± 0	10 ± 2	18 ± 2	5 ± 1	3 ± 1	6 ± 1	0 ± 0	0 ± 0	2 ± 1	3 ± 1

Table S1 Bioelectrocatalytic current responses obtained upon challenging different anodes, based on TTF-loaded MCPs and capped by the indicated compositions of the enzyme assemblies, with 180 mM sucrose in a N_2 -purged McIlvaine buffer solution. The reported currents correspond to the value obtained at $E=0.35 \text{ V vs. SCE}$ using cyclic voltammetry at a scan rate of 20 mV s^{-1} . The errors were derived from a set of $N=3$ experiments.